THE DEVELOPMENT OF SPANGOLD

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The underlying mechanisms of martensitic phase transformations in gold alloys have attracted a great deal of study. Whereas their technological exploitation in shape-memory devices has found only limited application, the *Spangold* concept introduces a novel application – that of using the transformation to decorate gold ornaments. This article examines the attributes of suitable alloys and the development of a prototype alloy for use in jewellery.

INTRODUCTION

The Spangold concept is described in a companion publication [1] and is the subject of recent patents applied for by Mintek [2]. In essence, Spangold refers to a family of gold alloys formulated to undergo a phase transformation. This change in the crystal structure, known in simple terms as a martensitic transformation, manifests itself as a change in the surface relief of the alloys. The modification of the surface texture gives rise to a decorative glitter, or 'spangle', which is intrinsic to the alloys, and gives them their name. The aesthetic properties of Spangold find application in jewellery.

While in principle the Spangold concept can be extended to embrace all the systems that exhibit martensite-like transformations, those transformations associated with intermetallic compounds of gold are of particular interest. This article examines some of the specific requirements for exploiting the Spangold effect for ornamental purposes and shows that, apart from the dictates of caratage and aesthetics, alloys based on intermetallic compounds can also be usefully engineered in terms of other properties, such as castability, density, and wear resistance. Although these alloys are extremely versatile, their properties can differ significantly from those of conventional jewellery alloys and, by their nature, require different manufacturing and finishing techniques.

BACKGROUND

The aesthetic properties of gold, revered for its deep yellow colour, have been the wellspring for much of the characterization work on gold alloys and compounds. The development of Spangold issues from an age-old fascination with the decorative nature of gold compounds.

Intermetallic compounds based on $AuAl_2$, were noted for their striking purple colour [3] as early as 1891. Intermetallic components are based around simple, but thermodynamically stable, stoichiometric combinations of the constituent elements. The diversity and range of gold compounds have been described in an extensive literature [4].

Martensitic phase transformations in discrete gold compounds were identified by Chang and Read [5] in the early 1950s. Since then, their discovery has evolved into the science of shape-memory alloys and related phenomena in a wide range of systems. Numerous potential shape-memory applications for gold-base alloys have been put forward, since they are perceived to have advantages in components where colour and resistance to corrosion and tarnishing are important. Whereas the original gold-cadmium compounds of Chang and Read were relatively brittle, and were studied in single-crystal form, a number of relatively malleable alloys have been identified subsequently. For example, the Fulmer Research Institute patented alloys containing between 40 and 60 per cent gold by mass and proposed their use in jewellery, citing applications such as the gripping of jewels in mounts [6, 7]. Recently new gold-base shape-memory alloys for use in ornamental items have been claimed by Japanese manufacturers [8, 9]. In these developments, interest focussed on the mechanical and shape-memory properties.

The Spangold concept exploits the martensitic phase transformation, common to shape-memory alloys, for decorative purposes. The phase transformation distorts the original crystal structure, and induces a surface relief pattern. Under ideal conditions. this is sufficiently pronounced to obtain dispersion of reflected light, giving the alloys their characteristic glitter. Not all martensitic transformations are suitable in this regard. The phase changes can yield a range of martensitic variants, depending on the alloy composition. In other systems. the mechanical, environmental, and optical properties of the alloys are not com- patible with jewellery applications.

A detailed review of the crystallographic theory of martensitic transformations is beyond the scope of this article. Instead, the focus is on the qualitative attributes of the phase transformations exploited in Spangold, and their application in a prototype alloy system.

GOLD ALLOYS FOR JEWELLERY

Gold alloys suitable for use in jewellery have certain minimum requirements, based on their intrinsic value and appearance. While some of these attributes may be obvious, they bear stating because the properties of the envisaged intermetallic compounds can be very dissimilar to those of conventional alloys. **Table 1** contains a list, by no means exhaustive, of what may be classified as *primary* and *secondary* properties.

Table 1

Properties of gold jewellery alloys

Primary	Secondary
Colour	Workability
Caratage	Castability
Inertness to environment	Strength/Wear resistance

Owing to the nature of bonding in intermetallic compounds, their intrinsic properties are frequently inappropriate for structural applications. Moreover

- while colour is of almost unique importance in gold alloys, not all gold alloys and intermetallic compounds exhibit any colour. Rather, the electronic structure normally gives rise to metallic silver or grey tones;
- intermetallic compounds usually have limited malleability, a restricted composition range, and can suffer from environmental degradation, such as 'intermetallic pest';
- owing to their high thermodynamic stabilities, intermetallics often have high melting ranges.

Furthermore the Spangold alloys must undergo a suitable transformation, which is manifest at the surface as macroscopic strain resulting in the necessary optical properties.

PHASE TRANSFORMATIONS IN GOLD ALLOYS

Only a relatively small number of metallic alloys undergo a martensitic phase transformation. In the simplest form, a martensitic phase transformation may be considered to be a displacive solid-state transformation, without diffusion. More accurately, the mechanism is described as 'invariant plane strain' and manifests itself macroscopically as a shape deformation of the surface. On a microstructural scale, the martensite appears as packets of lenticular laths, plates, or twins.

The non-ferrous martensites can be loosely classified into three groups, according to the description provided by Delaey *et al.* [10]. The alloy systems belonging to the *first group* are all terminal solid solutions based on elements that in the pure form exhibit an allotropic phase transformation. Those belonging to the *second group* have in common a parent body-centred cubic (*bcc*) beta phase, which is intermetallic. Finally the *third group* is characterised by a cubic-to-tetragonal (or orthorhombic) phase transformation. This deviation from a cubic unit cell is often small, and the transformed phases are sometimes referred to as quasi-martensites [10].

The gold alloys that exhibit a martensitic transformation generally, but not exclusively, derive from the class of alloys known as beta-phase electron compounds (*group two*). At elevated temperatures, the compounds exist as a *bcc* beta phase, which transforms to a martensitic phase under the appropriate cooling conditions. In most cases, the beta phase exhibits atomic ordering, in which case the martensite phase is also ordered.

Phase transformations that are phenomenologically akin to martensitic transformations, but are often treated separately in the literature, include the development of structural order in certain alloy systems. In particular, the ordering reactions of the compound AuCu have received a great deal of attention in this regard [11–14]. It is now rigorously known that Au-Cu alloys of roughly equiatomic composition form two complex ordered tetragonal or orthorhombic phases on cooling from the disordered face-centred cubic parent phase. Both of these ordering reactions give rise to characteristic relief effects on a polished surface, and generate internally twinned plates of the AuCu phase [11]. The mechanism of transformation necessarily requires relocation of neighbouring atoms. However, since the relocation does not contribute to the transformation shape change, the operative crystallographic theory has been argued to be consistent with a marsensitic shear transformation [14]. For the

purposes of this discussion, we therefore refer to the transformations in AuCu as being martensitic. In character, the AuCu system is most closely related to a *group three* martensite. The similarity between the ordering reaction in AuCu and a martensitic transformation also finds expression in other martensitic ordering reactions (Co-Pt, Mg-Cd, Fe_3Al) [15].

Our studies have shown that the shape deformation effect in AuCu alloys can be enhanced by ternary alloying. Since the AuCu phases centre around a gold composition of about 75 wt.% (or 18 carat), they form an admirable basis for the development of the Spangold concept in gold jewellery, and this system receives further attention here.

Finally, of peripheral interest is the phenomenon of transformation reactions that are confined to the surface region. The removal of transformation strains at the surface can cause a twinning reaction to a depth of some 7 to 10 nm beneath the surface. The structure of the surface martensite is reported to he very dependent on the surface orientation, and is unrelated to that of the bulk martensite, if indeed the alloy undergoes a bulk transformation [10]. Spontaneous phase transformations that are limited to the surface have been recognised in other alloys (Lovey *et al.* [16]). These are of interest regarding the Spangold concept, since they hold out the potential of combining the decorative effect with the properties of the base alloy. This also suggests the possibility of coating substrates with alloy films that undergo martensitic transformations.

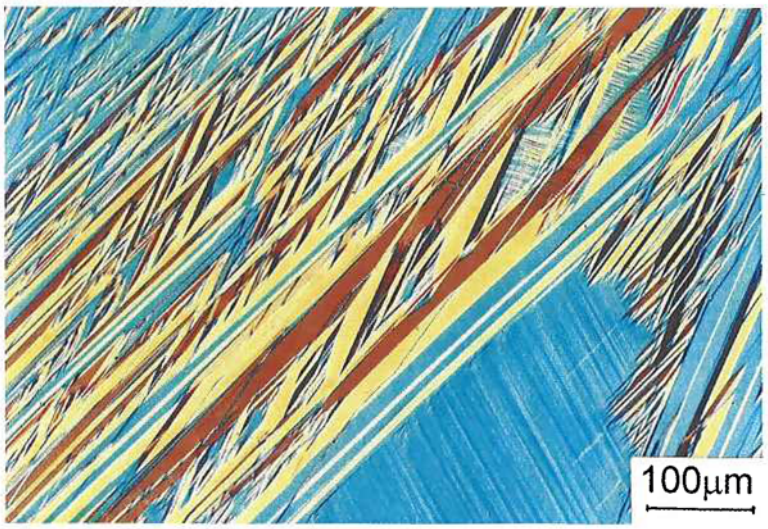


Figure 1

The characteristic 'basket-weave' structure of the martensite in copper-base alloys, shown for a Cu-Zn-Al-brass

CHARACTERIZATION OF MARTENSITIC STRUCTURES IN GOLD

The martensitic transformation of the parent phase usually occurs over a characteristic range of temperatures, commencing at the martensitic start (M_s) temperature, and proceeding to completion at the finish (M_f) temperature. Similarly, heating of the martensite phase progressively restores the parent phase, although, as will be seen, the morphology of the surface exhibits varying degrees of reversibility. In theory, the alloys can be cycled through the transformation an indefinite number of times.

Martensite structures may be distinguished on the basis of their internal microstructure. Broadly speaking, the martensites exhibit *internally faulted* or *internally twinned* structures. Copper-base martensites usually conform to a faulted structure and appear as plates in a 'basket-weave' pattern under the microscope. A typical example is shown in **Figure 1**.

In contrast, *internally twinned* martensites are identifiable by their strongly aligned twin-band structures. The intermetallic Au-Cd and Au-Mn alloys fall into this class. The transformations experience very little elastic constraint and entire grains can undergo transformation to a single martensite crystal instead of to a number of small discrete plates [17]. When nucleation occurs at several points within the grain, intersecting families of twins occur (**Fig. 2a**).

Characteristic martensitic structures, and the accompanying change in the relief of a polished surface, are illustrated in **Figure 2** for alloys of Au-Mn and Au-Ti. It will be apparent that a diverse range of physical structures occurs and that not all of these are detectable with the naked eye. Whereas some, like the copper-base alloys in **Figure 1**, exhibit a coarse structure with marked surface relief, the surface distortion wrought by other phase changes is on such a fine scale as to be visible only under a microscope.

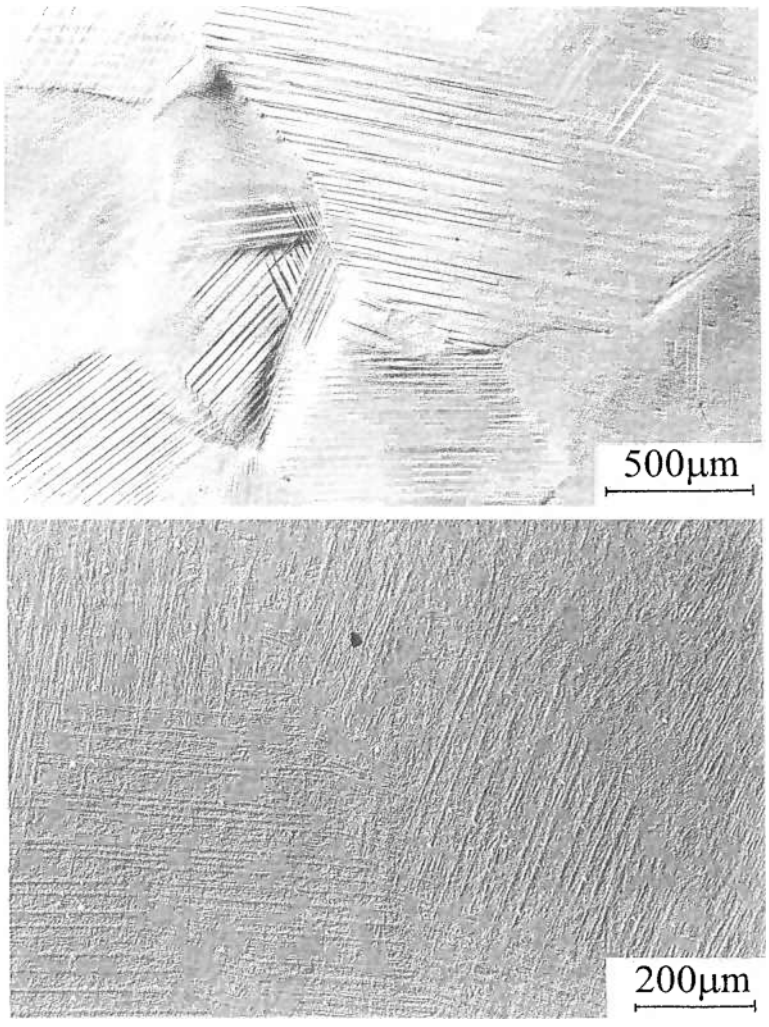
PHASE TRANSFORMATIONS IN THE Au-Cu SYSTEM

The phase transformations in the Au-Cu system give rise to features that are ideally suited to the Spangold concept, in that they occur at modest temperatures and the surface structures can be readily regenerated. The alloys also display some unique transformation characteristics. Consideration is given here to the microstructural development of the pseudo-binary Au-Cu-Al system, selected to have a fineness of nominally 18 carats, as a prototype of the Spangold concept.

As noted above, in alloys containing in the region of 75 wt.% gold, cooling from the random *fcc* parent phase leads to ordering of the $L1_0$ type below about 380 °C, and to the formation of an orthorhombic AuCu(II) phase between 380 and 410 °C. In the case of the $L1_0$ reaction, the surface relief is caused by mechanical twinning subsequent to ordering, but the AuCu(II) reaction tilts the surface as an ordered region grows from the cubic phase [15]. It has been noted [15] that the growth of the ordered plates as long bands parallel to a pseudo-habit plane closely matches the transformation characteristics of copper-zinc alloys. The plates possess an internally twinned structure, and have been postulated to grow by the gliding of transformation dislocations at a rate determined by the rate of ordering at the dislocations [14].

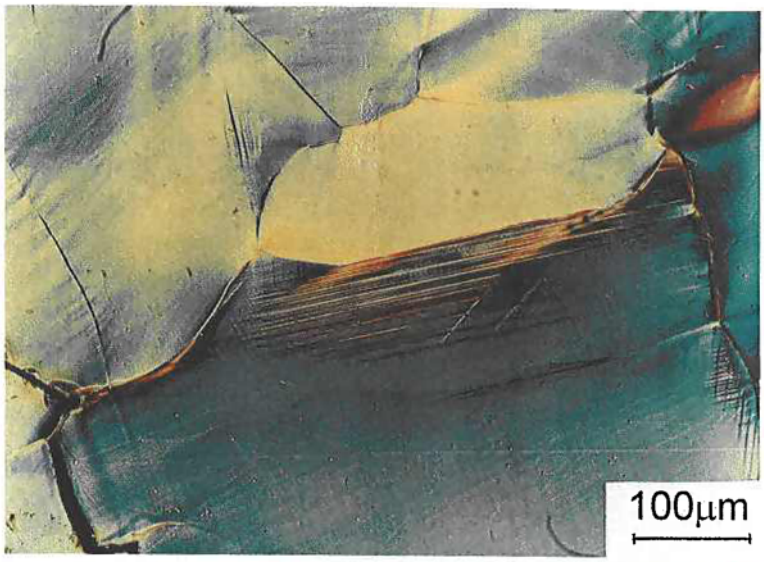
The mechanistic route giving rise to invariant-plane strain in AuCu alloys is therefore characterised by an ordering reaction that accompanies the martensitic shear transformation. The shape deformation consequently proceeds from the ordered intermetallic compound rather than the disordered parent phase, although for practical purposes the spangle is generated in a similar fashion, namely by cooling from above the ordering temperature.

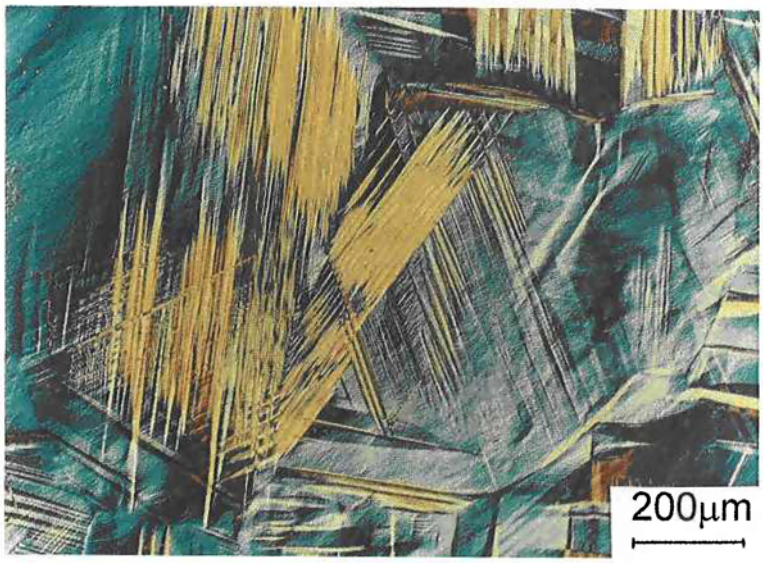
The effect of small additions of aluminium on the phase change in 18 carat Au-Cu alloys, as manifest on polished surfaces, is shown in **Figure 4**. Following identical heat treatments, aluminium additions cause a progressive change of the strongly aligned twin structure, from one of incipient twinning and tilting of the surface to a structure more closely resembling the broad bands found in the copper-base alloys. Relative to the AuCu-base alloy, additions of aluminium promote complete transformation, probably as a result of a shift in the phase boundaries, effectively enhancing the kinetics. At the same time, the surface relief is accentuated, which results in a more effective scattering of incident light. Thus, by appropriate alloying, the martensitic structure can he modified to exhibit more pronounced optical properties.

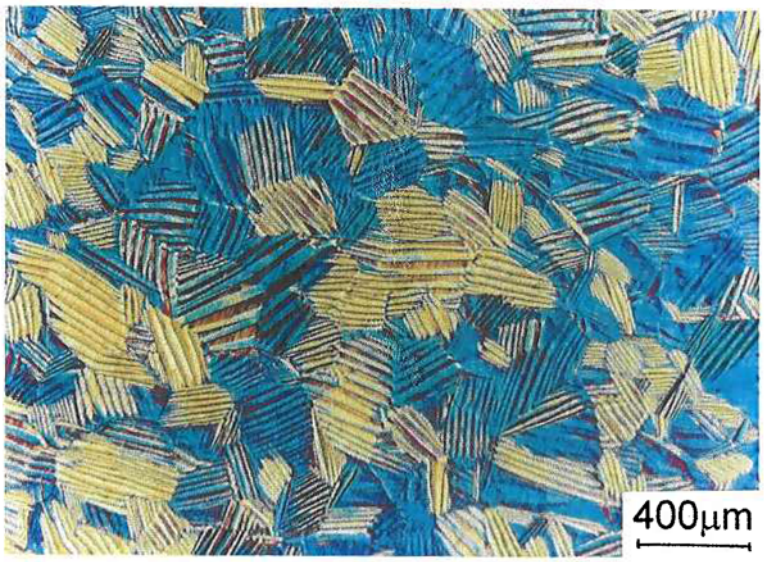


Figures 2a and b

Twinned martensitic structures in alloys based on Au-Mn (a), and Au-Ti (b)







Figures 3a, b and c

Variation of the martensitic structure as a function of aluminium content in 18 carat Au-Cu-Al alloys. Following identical heat treatments, the microstructural development shows
(a) incipient twinning and tilting of the surface,
(b) modification of the twin structure, and
(c) complete transformation with broad twin bands.

THE CONCEPT OF ANTI-SPANGLE

It will be understood that modification of the surface topography of the 18 carat Au-Cu-Al alloys can be brought about in two ways. If in the first instance, a polished surface of the parent phase is slowly cooled through the transformation temperature regime, the transformation distorts the surface, creating the desired spangle. If the spangle created by the transformation is now polished flat, the surface once again distorts if the alloy is heated back through the transformation temperature. In the latter case, the martensite is converted back to the parent phase, thus reversing the transformation and, in effect, reversing the original distortion. This gives rise to a microstructure that is optically similar to the martensitic structure, and which is designated 'anti-spangle' for convenience.

Under ideal conditions, the anti-spangle once again reverts to a smooth surface on cooling but, in practice, there is some constraint which prevents the plates from fully recovering the original relief. On cooling, new martensitic plates may nucleate as a result of the remnant 'anti-spangle' plates. Thus the surface topography may comprise a combination of the two effects. The faded remnant anti-spangle plates or twins can be discerned in the background of the transformed structure in **Figure 4**.

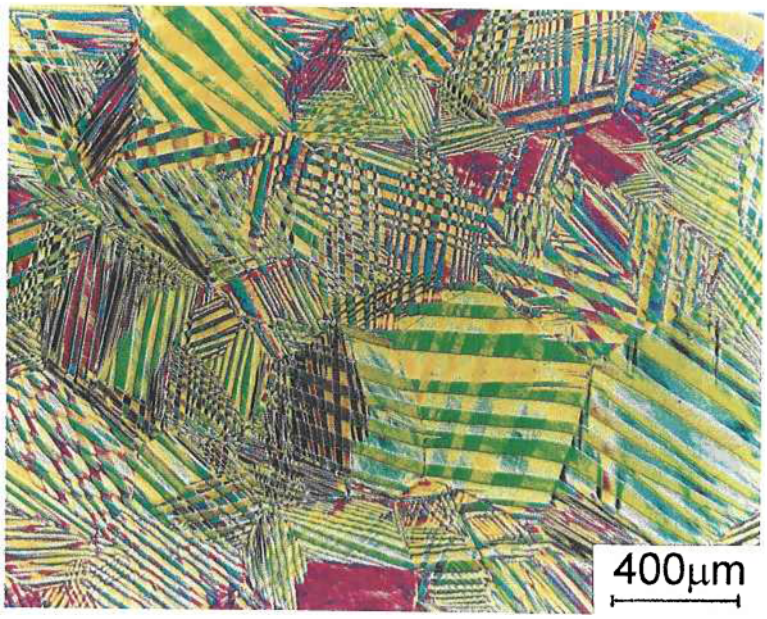


Figure 4

Complex 'anti-spangle' structure derived from superimposition of the martensitic structure on the reverse transformation during cycling

The hysteresis in the reverse transformation can be attributed to 'lattice invariant strain', or lattice defects such as twins, stacking faults and/or dislocations introduced by the transformation, and which tend to prevent complete reversibility. This leads to the development of an unusual surface morphology. Criss-crossing plates can give rise to a type of 'basket-weave' structure (**Fig. 4**), which accounts for the apparent anomaly of plates lying across one another. In effect, this further enhances the spangle.

The 'memory' capability of the alloys can be manifest in other ways. For example, the transformation can be induced by localised stresses, such as those that occur during machining.

When an alloy that has been quenched to retain the parent structure is machined before heating, stress-induced martensite gives rise to a surface relief that is superimposed on the transformed martensitic structure on heating. The result is a distorted plate structure that lacks the desirable definition of spangle, and results in the appearance of a wrinkled surface (**Fig. 5**).

OTHER PROPERTIES OF SPANGOLD ALLOYS

The properties of the intermetallic Spangold alloys can be modified in a number of other important respects. For the AuCu alloys, it has been seen that the addition of aluminium shifts the transformation reaction and also influences the transformation kinetics. However, small alloying additions also change

- the mechanical properties (**Fig. 6**),
- the castability (in terms of fluidity and melting point),
- the colour (**Fig. 7**).

Hardness of Ordered Compounds

It has long been recognized that there exists a maximum in the hardness of gold alloys that have been suitably heat-treated, at a composition of around 75 wt.% Au (see for example [18]) This has been linked to the development of structural order of the type discussed above, and constitutes an important mechanism for achieving higher strengths in gold alloys [19, 20].

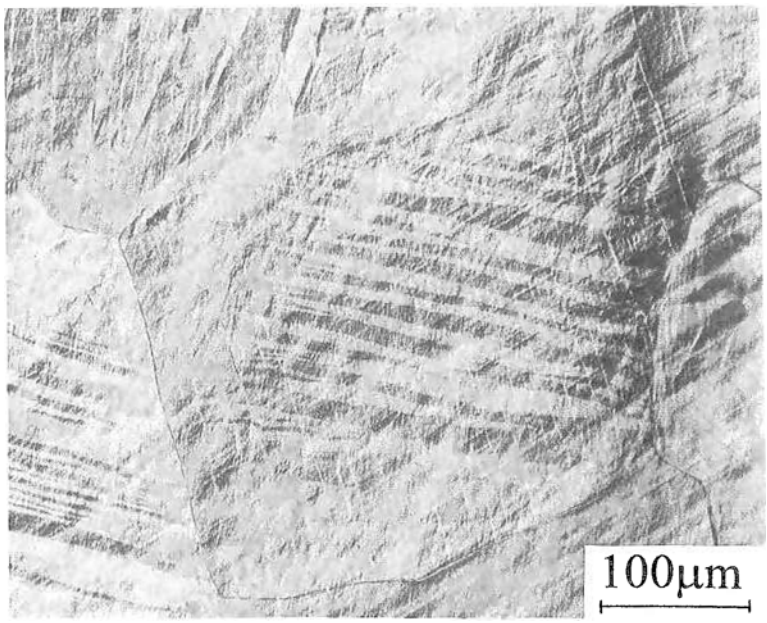


Figure 5

Distorted surface caused by partial stress-induced transformation

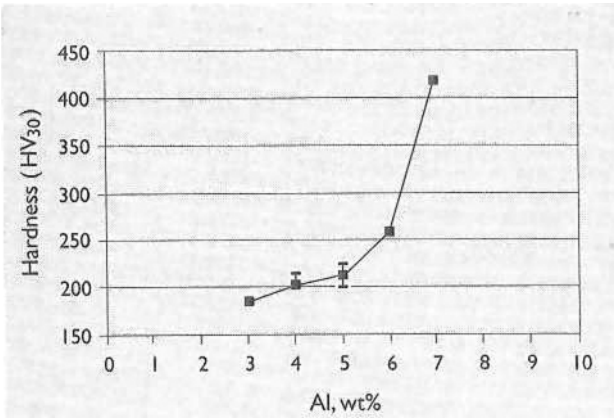


Figure 6

Hardness of transformed 18 carat Au-Cu-Al alloys as a function of composition

That an ordering reaction precedes or coincides with the transformation in Au-Cu-Al alloys seems certain from observations that the reaction can be suppressed by prolonged annealing in the disordered parent phase, followed by quenching. Transformation can then be induced by heating to within the temperature range 200 – 300 °C which suggests that thermal activation of the ordering reaction precedes trans- formation.

The attainment of higher hardnesses via the ordering reactions has important advantages. These include greater wear-resistance and the ability of the alloys to be finished with a high lustre.

Castability of the Intermetallics

As a result of their electronic configuration, the intermetallic compounds in general frequently exhibit unusual physical properties. One such property is their high degree of fluidity in the molten condition. This is a function of the free-electron to atom ratio, which approaches zero as the ratios of constituent elements approach stoichiometry.

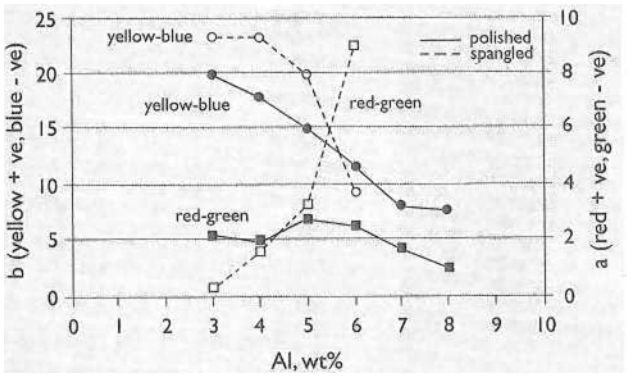
In practical terms, the width of the 'mushy' zone on the equilibrium phase diagram contracts until, at stoichiometry, an intermetallic compound may melt congruently.

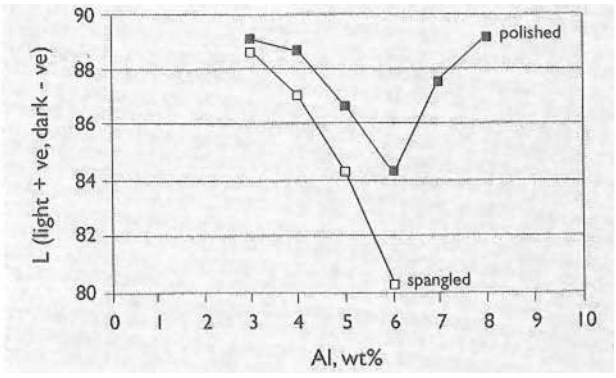
The low surface tension imparts good fluidity to the metal, and enhances castability. Thin, intricate shapes are therefore readily cast.

A further advantage of the Au-Cu-Al system is the relatively low melting range of the alloys, determined by differential thermal analysis to be between 715 and 770 °C, depending on composition. This further facilitates manufacture.

Colour

The deep yellow colour of gold is due to the absorption properties of its electronic structure. In effect, gold and copper have much higher reflectivities for the low-energy end of the visible spectrum, conferring the unique property of colour on them [21].





Figures 7a and b

Colour co-ordinates and reflectivity of 18 carat Au-Cu-Al alloys plotted in CIELab notation, showing the effect of composition:
(a) effect of Al content on co-ordinates a and b, (b) effect of Al content on co-ordinate L

Alloying additions to copper and gold progressively 'bleach' their colour by modifying the electronic band structure, shifting the reflected wavelengths to the ultra-violet region of the spectrum. The colour is also changed by the formation of an intermetallic compound, which produces an entirely new band structure. The intense 'purple gold' and 'blue gold' colours of $AuAl_2$ and $AuIn_2$ respectively, result from a rise in the reflectivity towards the violet end of the spectrum [22]. This causes the red and the violet wavelengths to be strongly reflected, resulting in a striking reddish-purple colour in $AuAl_2$.

The addition of copper to gold shifts the reflectivity to slightly lower energies, creating the colour of 'red' gold. It is therefore interesting to note that the replacement of copper with aluminium in the intermetallic AuCu-AuAl pseudo-binary leads to a shift in the reflected colour, namely from yellow to red to purple to white (**Fig. 7**). The progression appears to emulate the $AuAl_2$ compound. (From a consideration of the Au-Al phase diagram, it will be seen that $AuAl_2$ is a constituent phase at the copper-poor end of the pseudo-binary 18 carat series, but does not appear to play a role at the lower aluminium levels.)

As an additional feature of interest, it is worth noting the apparent shift in the colour brought about by the spangling transformation. The Au-Cu-Al system therefore joins the ranks of the coloured intermetallics. This effect has also been recognized in copper-base alloys, and forms the basis of several patents [23, 24].

APPLICATION OF SPANGOLD

The incorporation of the Spangold effect in selected jewellery items is shown in **Figures 8** and **9**. The Spangold is offset against conventional 18 carat gold, as well as a variety of other finishes such as red-ivory wood, rhodium-plating and precious stones. The vivid and scintillating contrast of the Spangold finish is eloquent testimony to the attractiveness of these gold alloys.

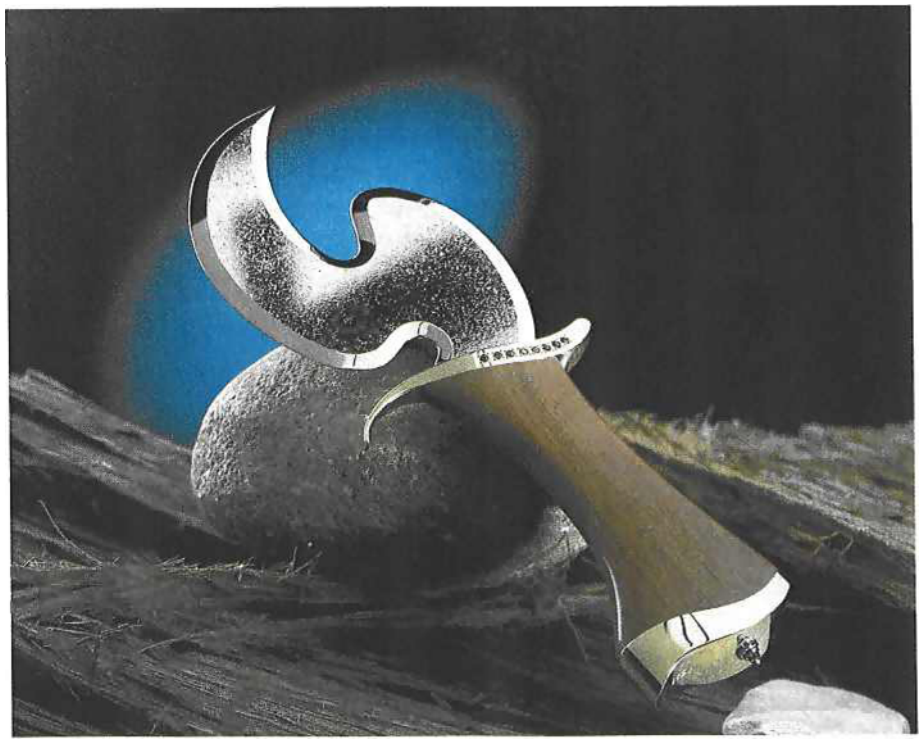


Figure 8

Exemple from the Spangold collection:
18 ct dagger, with 'red' Spangold blade, finished with red ivory wood, rubies, red tourmaline, and yellow gold

SUMMARY

The Spangold concept embodies a unique combination of attributes inherent in certain alloys. These include their spectacular transformation properties, colour, and variety of finishes.

The characterization of suitable transformation features led to the successful development of prototype Spangold alloys. In addition to exploiting their novel finish, the use of the prototype Spangold alloys in jewellery also realizes the practical application of structural gold base compounds.

Apart from their optical qualities, the Spangold alloys based on intermetallic com-

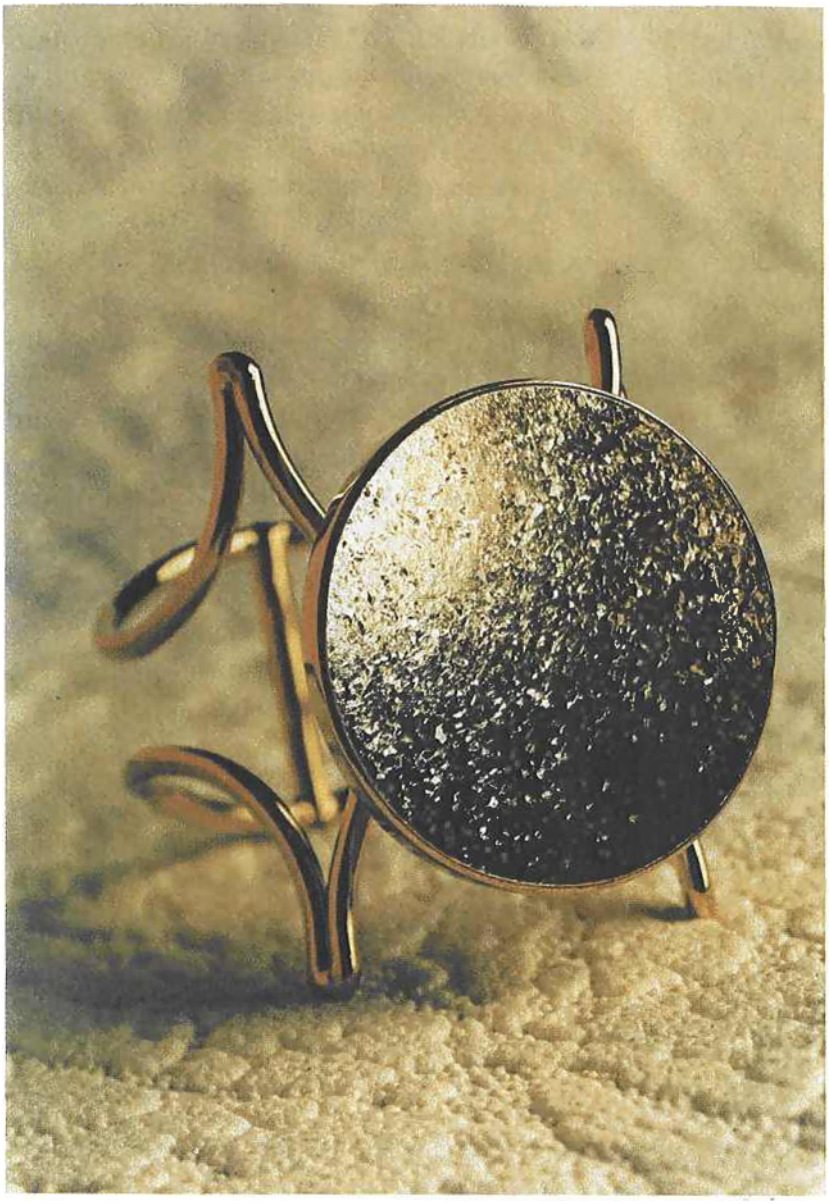


Figure 9
Exemple from the Spangold collection: Tension bracelet, finished with yellow gold

pounds can exhibit a number of other salient features pertinent to their application in jewellery. These include density, lustre, castability, and wear-resistance. These gold compounds possess a wide and novel range of properties and are likely to enjoy continuing interest.

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